

# Modeling and Simulation of an Emulsion Copolymerization Process

Sabrina Copelli<sup>\*a</sup>, Mario Dente<sup>b</sup>, Marco Derudi<sup>b</sup>, Giulia Bozzano<sup>b</sup>, Vincenzo Torretta<sup>a</sup>

<sup>a</sup>Università degli Studi dell'Insubria - Dip. di Scienza e Alta Tecnologia - Via G.B. Vico 46 - 21100 Varese - Italy

<sup>b</sup> Politecnico di Milano - Dip. di Chimica, Materiali e Ingegneria Chimica "G. Natta" - P.za Leonardo da Vinci - 20133

Milano - Italy

[sabrina.copelli@uninsubria.it](mailto:sabrina.copelli@uninsubria.it)

Radical emulsion copolymerization is one of the most widely diffused processes aimed to produce paints easy to use because of their low viscosity. At industrial scale, such processes require a high performance control of all the operating variables. Particularly, the repeatability of an emulsion polymerization process within narrow limits is one of the most desirable features because it allows for controlling also other important product qualities. Other important full plant requirements are the minimization of reactants dosing times and the preparation of a latex at the highest possible concentration. In this work, the first step of a complex industrial copolymerization process has been modeled. Since different monomer types are involved, it has been necessary to propose a complete set of rate constants for all the traditional steps of the radical emulsion reactions chain. These parameters have then been inserted in a system of ordinary differential equations expressing all balances and control actions aimed to simulate the full plant synthesis. Finally, the proposed model has been experimentally validated through the comparison with a reaction calorimetry test carried out in an indirectly cooled semibatch reactor (RC1, 1L, Mettler Toledo). Obtained results have confirmed the reliability of the theoretical model.

## 1. Introduction

Radical emulsion copolymerization is one of the most widely diffused processes aimed to manufacture several commercially important polymers. Many of these polymers are used as solid materials and therefore they must be isolated from the aqueous continuous phase after polymerization completion. In other cases the emulsion itself (also referred to as latex) is the final desired product.

At industrial scale, such processes require a high performance control of all the operating variables (such as dosing times of the involved reactants, surfactants, initiators and additives, reactor temperature, coolant flow rate, etc.). Particularly, the repeatability of the emulsion polymerization recipe is one of the most desirable features because it allows for controlling also other important product qualities as final solids content (that should be constant within  $\pm 1\%$ ), average particle size, latex viscosity and polymer average molecular weight (Erbil, 2000). Other important full plant requirements are the minimization of reactants dosing times (the process should be completed in the shortest possible time taking into account also safety problems associated to polymerization exothermicity) and the preparation of a latex at the highest possible concentration (up to 55% w/w of solid in the emulsion is desirable).

Because of all these critical features, a detailed modelling and simulation of such synthesis at industrial scale is not so easy to perform even if existing literature provides lots of reliable and complete kinetic schemes for copolymerization processes (e.g., Hutchinson and Wang, 2011). As a matter of fact, most of these models can be applied only to isothermal systems (runaway phenomena due to the loose of temperature control, frequently occurring at industrial scale, cannot be properly taken into account) and they do not face the problem of complex monomers dosing policies and cooling system time delays.

In this work, the first step (trigger) of a complex industrial copolymerization process has been modeled with the main aim of providing a versatile tool to simulate the effect of a variation of operating parameters on

the industrial process dynamics. Since different monomer types (butyl acrylate, styrene, acrylic acid and acrylamide) are involved in the synthesis, it has been necessary to propose a complete set of global rate constants (frequency factors  $A$  and activation energies  $E$ ) for all the traditional steps of the radical emulsion reactions chain (i.e. initiation, propagation, radicals termination for both combination and disproportionation, backbiting and long-chain branching, micelles seeding, etc...). These parameters have been then inserted in a system of ordinary differential equations, representing mass and energy balances, in order to reproduce all full plant recipe steps (e.g. loading of fluids, polymerizing, heating and cooling). Dosing strategies, temperature control modes (isothermal, isoperibolic, etc...), densities and volumes variations, radicals diffusion (inside and outside the micelle/polymer particles), homogeneous (in water) and micellar nucleation with polymer particles coagulation phenomena have been properly taken into account within the model.

Finally, all proposed parameters have been then experimentally validated through the comparison with a reaction calorimetry test carried out in an indirectly cooled semibatch reactor (RC1, 1L, Mettler Toledo) operated in both isoperibolic and isothermal temperature control mode. Obtained results have confirmed the reliability of the theoretical model.

## 2. Experimental

### 2.1 Reacting System

In the following it will be reported only the first step (trigger) of an industrial recipe for styrene/butyl acrylate emulsion copolymerization (final solid content of this step, about 20% w/w).

In order to perform a laboratory synthesis which is as close as possible to that one carried out at industrial scale, an RC1 equipment (MP06, 1 L, Mettler Toledo), indirectly cooled by means of an external jacket, has been used with the following operational list: (1) distilled water (W, continuous medium) and Disponil 72 (Disp, surfactant) are loaded in the reactor and, then, heated up to 75°C in 40 min activating an isothermal temperature control mode; (2) to allow for the formation of Disp micelles (that will contain the growing polymer chains), the mixture is kept at 75°C for about 1 h; (3) a pre-emulsion of distilled water, Disponil 72, acrylamide, acrylic acid, styrene and butyl acrylate is loaded one-shot in the reactor and, then, the temperature control mode is shifted to isoperibolic ( $T_{cool,set} = 80^\circ\text{C}$ ) providing a waiting time of 20 min to allow for the reactor and jacket temperatures equilibration; (4) sodium persulfate (NaPS) is dosed in 30 s through an automatic syringe; (5) a waiting time of about 30 min is provided to permit reaction completion; (6) temperature control mode is then shifted to isothermal ( $T_{set} = 80^\circ\text{C}$ ) for successive dosing. Reactants and reactor characteristics are summarized in Table 1.

Table 1: Process recipe and reactor characteristics for the free radical emulsion copolymerization of styrene/butyl acrylate thermally initiated by NaPS.

Initial Load		Dosed Stream		Cooling System
190 g	Water	5.4 g	Water	Jacket: external
14.1 g	Disponil 72			( $T_{cool,set} = 80^\circ\text{C} - T_{set} = 80^\circ\text{C}$ )
1.1 g	Acrylamide	0.3 g	Sodium Persulfate	Coolant: silicon oil
0.7 g	Acrylic Acid			Nominal Volume: 1 L
13.7 g	Styrene			( $UA$ ) <sub>0</sub> = 3.15 W/K
14.8 g	Butyl Acrylate			( $UA$ ) <sub>ext</sub> = 0.32 W/K

### 2.2 Instruments and Techniques

Differential Scanning Calorimetry (DSC) is a calorimetric technique that allows for substances thermochemical characterization by comparing the thermal behavior of a sample with that one of a reference (Copelli et al., 2011). Particularly, the instrument is able to record the rate at which the sample develops or absorbs heat during a transformation and generate characteristic diagrams that report the heat power exchanged between sample and reference versus temperature or time. In this work an isothermal (sample holder: stainless steel, medium pressure, Viton/120  $\mu\text{L}$ /closed/nitrogen atmosphere; sample investigated temperature, 75°C) DSC test has been carried out in order to determine the copolymerization reaction enthalpy ( $\Delta h_{rxn} = 6.8024\text{e}7 \text{ J/kmol}$ ).

Reaction Calorimeter RC1 is a laboratory reactor of 1 L capacity particularly useful to estimate model and kinetic parameters that can be used even to simulate processes operated at industrial scale. It is equipped with an external jacket to heat or cool the reaction mass, a thermocouple and a calibration probe, which is necessary in order to determine mass specific heat capacities ( $c_p$ ) and global heat transfer coefficients ( $UA$ ). Moreover, in the RC1 evaluation software it is possible to take into account the variation of  $c_p$  and  $UA$

parameters by superimposing different constraints and ranging modes. For the case here considered, as the overall heat transfer coefficient varies from  $U_0$  to  $U_f$  (because of the reacting mixture viscosity increase), it has been superimposed that the overall heat transfer coefficient varies linearly with the stirrer torque ( $To$ ) collected by the RC1.

### 3. Model

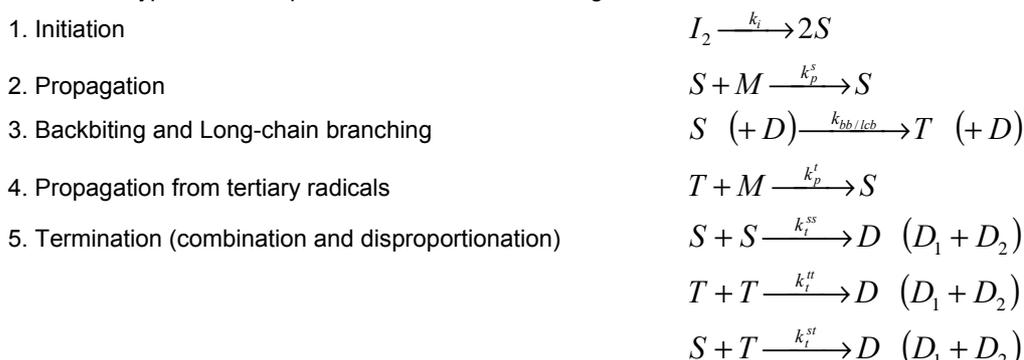
In the following it will be presented the mathematical model used to simulate styrene/butyl acrylate emulsion copolymerization process at both industrial and RC1 scale.

#### 3.1 Kinetic Scheme

As it can be easily observed from the recipe reported in Table 1, four different monomers are involved into the synthesis; acrylamide and acrylic acid being present in very reduced amounts. Considering the most simple reactions chain (initiation, propagation and termination), at least 16 propagation and 9 termination kinetic constants are needed to simulate the complete kinetic scheme. Such a relevant number of parameters, whose values must be experimentally validated, is practically useless when a complex industrial synthesis, constituted by several temperature setpoint changes, non linear dosing policies and poor cooling efficiency, has to be simulated. In fact, thermal effects related to both reactions exothermicities and heat transfer, which are dominant at industrial scale, make the complete kinetic scheme practically unsolvable. For such a reason, in this work, it has been decided to use a kinetic approach that will be referred to as "pseudo-homopolymer approach".

Particularly, all monomers are considered as a single one having both reactive (kinetic parameters are directly estimated through a fitting procedure using the experimental RC1 data) and physico-chemical properties (e.g. densities, molecular weight and solubility) which are calculated as an average (weighted on the amounts of monomers used in the recipe) of those of all the monomeric species (standard mixing rules have been employed).

Under this hypothesis it is possible to write the following kinetic scheme:



where  $I$  is the initiator species (in this case, NaPS),  $S = \sum S_n$  and  $T = \sum T_n$  are pseudo-radicals which represent, respectively, all radical species of type  $s$  (secondary or terminal) and  $t$  (tertiary or mid-chain) independently of their chain length  $n$  (Terminal Kinetic Model, TMK; Hagiopol, 1999),  $M$  is the pseudo-monomer and  $D$  represents a dead polymer chain (no molecular weight distribution analysis has been considered according to the TMK theory). Moreover, in such a simplified kinetic scheme backbiting ( $bb$ ) and long-chain branching ( $lcb$ ) have been merged into a single contribution in order to further decrease the number of parameters to be theoretically estimated and, then, experimentally validated.

#### 3.2 Polymer Particles: Growth and Dimensions

An emulsion polymerization takes place over a number of steps, where various chemical and physical events occur simultaneously during the process of particle formation and growth (Nomura et al., 2005). Particularly, particle formation takes place when either: (1) a free radical in the aqueous phase enters a monomer-swollen emulsifier micelle and propagation proceeds therein (micellar nucleation); (2) the chain length of a free radical growing in the aqueous phase exceeds its solubility limit and precipitates to form a particle nucleus (homogeneous nucleation), or; (3) a free radical growing in the aqueous phase enters a monomer droplet and propagation proceeds therein (droplet nucleation, not considered in this work because all monomers are already emulsified when the initiator dosing is started).

However, if the resultant polymer particles are not stable enough, the final number of polymer particles produced, regardless of the mechanism of particle formation, is determined by coagulation between the existing particles (coagulative nucleation). In this work, micellar and homogeneous nucleation (from both  $s$

and  $t$  radicals) together with coagulative nucleation have been properly taken into account through the following equation expressing the average number of growing polymer particles:

$$\frac{dN_p}{dt} = k_{nucl,mic} N_{mic} ([S]_w + [T]_w) + k_{nucl,omo}^s N_a V_w [S]_w + k_{nucl,omo}^t N_a V_w [T]_w - k_{coal} N_p^2 \quad (1)$$

where  $N_p$  is the average number of growing polymer particles, -;  $k_{nucl,mic}$  is the micellar nucleation rate constant (independent of the radical type),  $m^3/(kmol \text{ s})$ ;  $[S]_w$  and  $[T]_w$  are the molar concentration of, respectively,  $s$  and  $t$  radicals in water,  $kmol/m^3$ ;  $N_{mic}$  is the average number of micelles, -;  $k_{nucl,omo}^{st}$  is the homogeneous nucleation rate constant,  $1/s$ ;  $N_a$  is the Avogadro's number,  $6.022e26 \text{ -/kmol}$ ;  $V_w$  is the water volume (variable during the process because of the dosing),  $m^3$ ;  $k_{coal}$  is the coagulative nucleation constant,  $1/s$ . Concerning the process of particle growth, various chemical and physical events occur in both aqueous and particle phases. It is well known that polymerization takes place almost exclusively in the polymer particles phase, wherever free radicals have entered. Smith and Ewart (1948) were the first to establish a quantitative description of particles formation and growth in an emulsion polymerization process. In this work, a global non-stationary numerical approximation based on Smith-Ewart theory has been used to evaluate the average number of radicals (both  $s$  and  $t$  type) per particle,  $n_s$  and  $n_t$ . The resulting equations are:

$$\frac{dn_s}{dt} = r_p^t v_p N_a - 2r_t^{ss} v_p N_a - r_t^{st} v_p N_a - r_{bb/lcb} v_p N_a + r_{diff,wp}^s s_p N_a - r_{diff,pw}^s s_p N_a \quad (2)$$

$$\frac{dn_t}{dt} = -r_p^t v_p N_a - 2r_t^{tt} v_p N_a - r_t^{st} v_p N_a + r_{bb,lcb} v_p N_a + r_{diff,wp}^t s_p N_a - r_{diff,pw}^t s_p N_a \quad (3)$$

where  $r_p^t$  is the rate of propagation from tertiary radicals,  $kmol/(m^3 \text{ s})$ ;  $v_p$  is the average volume of a polymer particle,  $m^3$ ;  $r_t^{ss}$  is the rate of termination of two  $s$  radicals,  $kmol/(m^3 \text{ s})$ ;  $r_t^{st}$  is the rate of termination of an  $s$  radical with a  $t$  one,  $kmol/(m^3 \text{ s})$ ;  $r_{bb/lcb}$  is the global rate of backbiting and long-chain branching,  $kmol/(m^3 \text{ s})$ ;  $r_{diff,wp}^s$  is the diffusion rate of  $s$  radicals from water to the growing polymer particle,  $kmol/(m^2 \text{ s})$ ;  $s_p$  is the average surface of a polymer particle,  $m^2$ ;  $r_{diff,pw}^s$  is the diffusion rate of  $s$  radicals from the growing polymer particle to water,  $kmol/(m^2 \text{ s})$ ;  $r_t^{tt}$  is the rate of termination of two  $t$  radicals,  $kmol/(m^3 \text{ s})$ ;  $r_{diff,wp}^t$  is the diffusion rate of  $t$  radicals from water to the growing polymer particle,  $kmol/(m^2 \text{ s})$ ;  $r_{diff,pw}^t$  is the diffusion rate of  $t$  radicals from the growing polymer particle to water,  $kmol/(m^2 \text{ s})$ .

As a consequence, the average volume of a single growing polymer particle can be evaluated by either equation (4), if there are monomer droplets, or equation (5), if there are no more monomer droplets:

$$\frac{dv_p}{dt} = k_p^s \frac{\varepsilon_{mp}^* \rho_M}{1 - \varepsilon_{mp}^* \rho_P} \frac{n_s}{N_a} + k_p^t \frac{\varepsilon_{mp}^* \rho_M}{1 - \varepsilon_{mp}^* \rho_P} \frac{n_t}{N_a} \quad (4)$$

$$\frac{dv_p}{dt} = k_p^s PM_M \left( \frac{1}{\rho_P} - \frac{1}{\rho_M} \right) \frac{n_s}{N_a} [M]_p + k_p^t PM_M \left( \frac{1}{\rho_P} - \frac{1}{\rho_M} \right) \frac{n_t}{N_a} [M]_p \quad (5)$$

where  $k_p^s$  is the kinetic constant for secondary radicals propagation reaction,  $(m^3 \text{ s})/kmol$ ;  $\varepsilon_{mp}^*$  is the monomer volumetric fraction in the growing polymer particle, -;  $\rho_M$  and  $\rho_P$  are, respectively, the monomer and polymer density,  $kg/m^3$ ;  $k_p^t$  is the kinetic constant for tertiary radicals propagation reaction,  $(m^3 \text{ s})/kmol$ ;  $PM_M$  is the monomer molecular weight,  $kg/kmol$ ;  $[M]_p$  is the monomer molar concentration in the growing polymer particle,  $kmol/m^3$ .

### 3.3 Material Balance Equations

In order to completely characterize the kinetic scheme, the following material balance equations are presented:

initiator:

$$dn_I/dt = F_I - r_i V_w \quad (6)$$

emulsifier:

$$n_E - [E]_{w,sat} V_w + s_{mic} \cdot N_{mic} / a_s + s_p \cdot N_p / a_s = 0 \quad (7)$$

radicals of type  $s$  and  $t$  in the aqueous phase (that are not reported because are perfectly complementary with respect to radicals balance equations in the growing polymer particles) and monomer:

$$dn_M/dt = -(r_p^s + r_p^t)v_p N_p \quad (8)$$

For the equations (6) to (8):  $n_I$  is the initiator number of moles, kmol;  $F_I$  is the initiator molar flow rate, kmol/s;  $r_i$  is the rate of initiator thermal decomposition, 1/s;  $n_E$  is the emulsifier total number of moles, kmol;  $[E]_{w,sat}$  is the Critical Micellar Concentration (CMC) in water, kmol/m<sup>3</sup>;  $s_{mic}$  is the average micelle surface, m<sup>2</sup>;  $a_s$  is the total area covered by 1 kmol of emulsifier, m<sup>2</sup>/kmol;  $n_M$  is the monomer number of moles, kmol; must be written.

### 3.4 Mixing Rules and Global Density

In order to evaluate the overall liquid volume, it has been hypothesized that: 1) simple additivity of volumes (ideal liquid solution) occurs; 2) densities are quite constant with temperature; 3) there is a volume contraction whenever monomer converts to polymer. The resulting volume equation is:

$$dV/dt = dV_{dos}/dt - \alpha V_{M,TOT} d\zeta_M/dt \quad (9)$$

where  $V$  is the liquid volume, m<sup>3</sup>;  $V_{dos}$  is the volume dosed until time  $t$ , m<sup>3</sup>;  $\alpha$  is the volume contraction factor, -;  $V_{M,TOT}$  is the total monomer volume, m<sup>3</sup>;  $\zeta_M = (n_{M,TOT} - n_M)/n_{M,TOT}$  is the monomer conversion, -;  $n_{M,TOT}$  is the total number of moles of pseudo-monomer, kmol. Consequently, it is easy to estimate an overall liquid density using the following global material balance equation:

$$d\rho/dt = (\rho_{dos}/V) \cdot dV_{dos}/dt - (\rho/V) \cdot dV/dt \quad (10)$$

where subscript  $dos$  refers to the dosing stream.

### 3.5 Energy Balances and Control Equations

Finally, it is necessary to write energy balance equations on both the jacket and the reactor:

$$(\rho_{cool} c_{p,cool} V_{cool}) dT_{cool}/dt = \rho_{cool} c_{p,cool} Q_{cool} (T_{cool,in} - T_{cool}) + UA(T - T_{cool}) \quad (11)$$

$$\rho V c_{p,mix} \frac{dT}{dt} = \frac{dV_{dos}}{dt} \rho_{dos} c_{p,dos} (T_{dos} - T) + (-\Delta h_{rxn}) \frac{dn_M}{dt} - UA(T - T_{cool}) - UA_{ext}(T - T_{amb}) \quad (12)$$

where  $T$  is the temperature, K;  $c_p$  is the mass specific heat capacity, J/(kg K);  $Q$  is the volumetric flow rate, m<sup>3</sup>/s;  $\Delta h_{rxn}$  is the molar reaction enthalpy, J/kmol; subscript  $cool$  refers to the coolant (or jacket), subscript  $in$  refers to an inlet stream; suitably complemented by control equations expressing reactor temperature control mode (in this case, isoperibolic = constant coolant temperature):

$$dT_{cool,in}/dt = -K_p \cdot [dT_{cool}/dt - K_i^{-1} \cdot (T_{cool,set} - T_{cool})] \quad (13)$$

where  $K_p$  is the temperature controller static gain, -;  $K_i$  is the reset time, s; subscript  $set$  refers to the setpoint; and dosing policy (in this case, constant feeding rate):

$$\begin{cases} dV_{dos}/dt = V_{TOT,dos}/t_{dos} & 0 \leq t < t_{dos} \\ dV_{dos}/dt = 0 & t \geq t_{dos} \end{cases} \quad (14)$$

## 4. Results

Equations 1-14 must be solved simultaneously in order to simulate either the industrial or the laboratory (RC1) styrene/butyl acrylate copolymerization process. Particularly, it has been necessary to propose theoretical values for all the parameters involved in the previously presented equations basing on both group contributions theory (propagation, termination and backbiting/long-chain branching kinetic constants) and innovative approaches for the description of all physical phenomena (particularly, homogeneous and coagulative nucleation). In this work, only a brief list of the most important estimated parameters will be reported (see Table 2). A complete description of all the estimation techniques will be reported in future works.

By inserting all the parameters reported in Table 2 and then solving equations 1-14, it has been possible to simulate a synthesis carried out in an RC1 equipment following the operational list presented in section 2.1 and the recipe reported in Table 1.

Table 2: Constitutive model and kinetic parameters for the free radical emulsion copolymerization of styrene/butyl acrylate. All the values have been theoretically estimated and, then, adjusted basing on the best fitting of the isoperibolic RC1 curve reported in Figure 1.

$A_i$	2.40e16 (1/s)	$A_p^t$	3.10e7 (m <sup>3</sup> s/kmol)	$k_{nucl,omo}^s$	1.33e-1 (1/s) at 343 K
$E_i$	1.50e5 (J/mol)	$E_p^t$	4.40e4 (J/mol)	$k_{nucl,omo}^t$	7.98e-4 (1/s) at 343 K
$A_{bb,icb}$	3.19e9 (m <sup>3</sup> s/kmol)	$A_i^{ss}$	4.00e8 (m <sup>3</sup> s/kmol)	$k_{nucl,mic}$	6.20e4 (m <sup>3</sup> /kmol s) at 343 K
$E_{bb,icb}$	4.60e4 (J/mol)	$A_i^{tt}$	3.00e7 (m <sup>3</sup> s/kmol)	$k_{coal}$	1.20e-28 (1/s)
$A_p^s$	3.80e7 (m <sup>3</sup> s/kmol)	$A_i^{st}$	1.00e8 (m <sup>3</sup> s/kmol)	$k_{diff,wp}$	2.81e-2 (m/s) at 343 K, t=0 s
$E_p^s$	3.00e4 (J/mol)	$E_i^{tt/ss/st}$	1.50e4 (J/mol)	$k_{diff,pw}$	2.74e-4 (m/s) at 343 K, t=0 s

Comparison between experimental and theoretical results is reported in Figure 1, where both reactor temperature (A) and jacket temperature (B) vs. time profiles can be visualized.

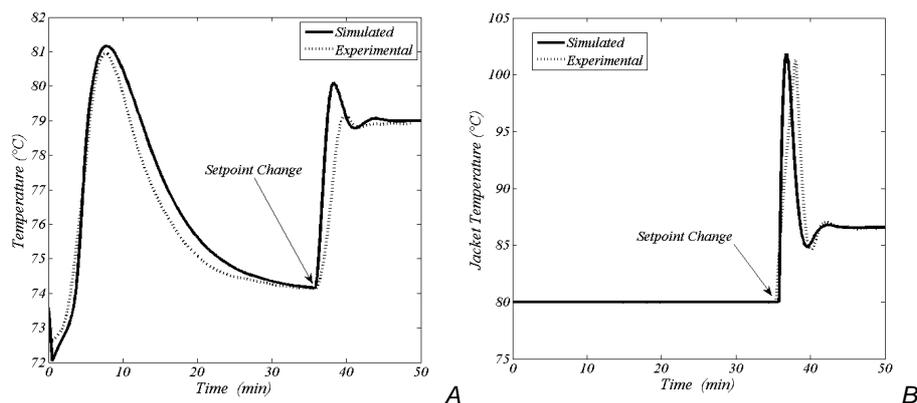


Figure 1: Comparison between experimental (dotted) and simulated (continuous) reactor temperature (A) and jacket temperature (B) vs. time profiles (see Table 1 and Table 2).

As it can be observed from Figure 1, a good agreement between experimental data and theoretical predictions has been achieved (even for what concern temperature setpoint change, see Figure 1B).

## 5. Conclusion

In this work, a phenomenological and computational model aimed to simulate the industrial synthesis of a styrene/butyl acrylate emulsion copolymerization has been developed. Such a theoretical model is able to reproduce a complex operational list, such as that one followed at the full plant scale, with a high degree of reliability thanks to a simplified but complete description of all the involved physico-chemical phenomena. This feature is confirmed by a good agreement between laboratory experimentation and simulated results.

## Acknowledgements

The authors wish to express their gratitude to Icap Sira Spa for financial support and to L. Gigante, C. Pasturezzi, C. Sala Cattaneo and M. Raboni for a part of the laboratory experimentation.

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